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Stereochemical Features *versus* Magnetic and Spectral Data on Iron(III) Complex with *p*-Dimethylamino-9-anthracyl Glyoxal Anil

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A new complex of Iron(III) with DIMAGA (p-dimethylamino-9-anthracyl glyoxal anil) with the composition $[Fe(C_{24}H_{20}N_2O)_2(Cl_2)]Cl$ *has been isolated and its structure is established on the basis of chemical analysis, molecular conductivity, magnetic moment and electronic spectra in nujol mull solvent. Relevant ligand field parameters and infra-red data are also discussed.*

Introduction

In recent years the octahedral complexes of DIMAGA[1] with various transition metal ions[2] have aroused much interest because of their interesting and significant conclusions which are discussed in this communication. However many low as well as high spin complexes of Iron(III) are known, but there is controversy among the workers[3,4,5] about the spectral and magnetic properties of these complexes.

In this paper the effect of ligand structure on the stereochemical and electronic properties of an Iron(III) complex with DIMAGA has been thoroughly investigated by chemical analysis, magnetic measurements and spectral (visible and infra-red) studies. Relevant ligand field parameters are also discussed at length.

Experimental

Chemicals of A.R. grade are used throughout. The electronic spectrum of the complex was recorded in non-aqueous medium at room temp. using a Hilger Uvispeck Spectrophotometer.

Infra-red spectra of the metal complex were recorded on a Perkin–Elmer Infra-red Model 137 in KBr pellets, whereas the spectra in the far infra-red region (16–40 μ) were recorded on a Beckman I.R. SA Spectrophotometer fitted with CsBr prism using nujol mull as solvent.

The magnetic susceptibility measurements on powder form of the complex were carried out at room temp. using Guoy's balance. Mercury(II) tetrathiocyanato cobaltate, $HgCo(CNS)_4$ ($Kg = 16.44 \times 10^{-6}$ C.G.S. units at 20° C) was used as calibrating agent.

Preparation and Isolation of the Complex Dichloro-bis(p-Dimethylamino-9-anthracyl glyoxal anilato) iron(III) Chloride

A dark violet coloured solution was obtained by mixing one mol of acetone solution of ferric chloride with two mol of DIMAGA. On concentration in a vacuum dessiccator a violet coloured complex was obtained. Crystals of the complex were washed thoroughly with acetonitrile and dried *in vacuo* at room temperature.

Molar conductance of the complex in DMF reveals its uni–univalent nature (M = 113.16 mhos in $10^{-3}M$ solution). *Anal.* Calcd. for $[Fe(C_{24}H_{20}N_2O)_2(Cl_2)]Cl$: C, 66.48; H, 4.61; N, 6.48; Cl, 12.29; Fe, 6.46%. Found: C, 65.80; H, 4.52; N, 6.38; Cl, 12.00; Fe, 6.37%.

On adding alcoholic silver nitrate solution to the isolated complex, a white curdy precipitate was obtained, indicating the presence of ionic chlorine outside the coordination sphere. Calcd.: Cl, 4.09%. Found: Cl, 3.94%. Magnetic measurements, electronic spectral data and relevant ligand field parameters are recorded in Tables I, II and III respectively.

TABLE I. Magnetic Measurements.

Compound	Temp.	$\chi_m \times 10^{-6}$ c.g.s. units	μ_{eff} (B.M.)		No. of Unpaired Electrons
			Obs.	Calcd.	
$[Fe(C_{24}H_{20}N_2O)_2(Cl_2)]Cl$	300° C	12134.0	5.4	5.92	5

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TABLE II. Electronic Spectral Data.

Compound	Medium	Observed bands, cm^{-1}	Assignments
$[Fe(C_{24}H_{20}N_2O)_2(Cl_2)]Cl$	Acetone	14000	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$
		19000	$^6A_{1g} \rightarrow {}^4T_{2g}(G)$
		24350	$^6A_{1g}$ (*d–d*) Transition $(t_{2g}-\pi^*)$
		27400	$(\pi-e_g)$ Charge Transfer
		38000	$(\pi-\pi^*)$ Charge Transfer

TABLE III. Relevant Ligand Field Parameters.

Compound	10 Dq, cm^{-1}	B, cm^{-1}	β	G	λ	C, cm^{-1}
$[Fe(C_{24}H_{20}N_2O)_2(Cl_2)]Cl$	14000	1276	0.98	1.52	338	5104

Discussion

Magnetic Studies

The experimental findings show that the complex compound consists of one mol of iron and two mol of the ligand (M:L = 1:2). In an octahedral environment, Iron(III) with d^5 configuration forms either higher spin type complexes under the influence of weak ligand fields containing five unpaired electrons (5.70–6.05 B.M.)[6] or low spin type under the influence of strong fields, containing only one unpaired electron giving the magnetic moment value of 2.3–2.4 B.M., a value which is larger than the spin only value for one unpaired electron[7]. In high spin, spin free outer orbital, weak field complexes, electrostatic bonding is believed to occur[8], while in the low spin, spin paired inner orbital, strong field complexes 3*d* orbitals also take part in bond formation giving covalent character to the bonds[8].

In the present Iron(III) complex under discussion, the value of magnetic moment observed is 5.4 B.M. which is in agreement with other high spin octahedral Iron(III) complexes.

The Electronic Spectra

The electronic ground state for Fe(+3) (d^5 ion) is ^6S. In the high spin octahedral complexes the ground state is $^6A_{1g}$ since this is the only sextet level present, hence other absorption bands present must be spin forbidden. In the electronic spectra of the complex five bands are observed at 14000 ($\varepsilon = 2.2$); 19000 ($\varepsilon = 1.8$); 24350 ($\varepsilon = 1.5$); 27400 ($\varepsilon = 1.2$) and 38000 cm^{-1} ($\varepsilon = 0.8$) which are tentatively assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ followed by $^4T_{2g}(G)$, *d–d* transition and other two charge transfer bands, because there exists a difference of opinion among the various workers[5]. The spectrum may be fitted to the Tanabe–Sugano diagram and to the transition given by Jorgensen[9, 10], Rabinowich and Stockmayer[11] and also by Kiss[12]. A complete analysis of the absorption spectrum of Fe^{+3} has not been obtained[13]. An attempt towards a theoritical explanation has been put forward by Naiman[14], but he also experienced difficulty as this ion complex possesses some extremely strong charge transfer bands which make the identification rather uncertain.

The value of 10 Dq has been calculated directly from the transition $^6A_{1g} \rightarrow {}^4T_{1g}(G)$ and from the ratio Dq/B = 1.1; the value of Racah's interelectronic repulsion parameter has been calculated to be 1276 cm^{-1} as against 1300 cm^{-1} in the free gaseous ion[13]. A more intense absorption band occurring at energies greater than 30000 cm^{-1} is generally assigned to $\pi-\pi^*$ transition, which in the present case occurs at 38000 cm^{-1}. The two lower bands in the region 23000 to 25000 cm^{-1} and 27000–28000 cm^{-1} have been assigned to $t_{2g}-\pi^*$ and $\pi-e_g$ transitions respectively. The values of energies $\pi-t_{2g}$ and $e_g-\pi^*$ can be calculated from the following relationships by knowing the energies of the observed transitions.

$$(\pi-e_g)-\Delta = \pi-t_{2g} \text{ in kK}$$

$$(t_{2g}-\pi^*)-\Delta = e_g-\pi^* \text{ in kK}$$

Further, for one electron molecular orbital, the sum of $\pi-t_{2g}$, $t_{2g}-e_g$ and $e_g-\pi^*$ in kK should be equal to the $\pi-\pi^*$ transition energy, which in the present case is found to be 37.75 kK. Since the difference between the observed (38.00 kK) and calculated (37.75 kK) is negligible, the calculated and observed band energies are in close agreement.

The value of two Condon–Shortley repulsion parameters f^2 and f^4 are related to B and C as given in the equation

$$C = \frac{35f^4}{441} \quad \text{(i)}$$

$$B = \frac{f^2}{49} - \frac{5f^4}{441} \quad \text{(ii)}$$

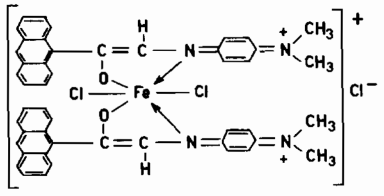
According to Rosengarten[15] the values of f^2 and f^4 for Fe^{+3} ion are 80.93 and 50.27 kK respectively. In the present complex these values are considerably increased to 98.19 and 64.31 kK which may be explained by the expanded radial functions for the *d* electrons[5].

I.R. Spectra

The point of attachment of the ligand with the metal ion could be confirmed by studying the infra-red spectrum of the ligand and the isolated chelates.

The strong band appearing at 1685 cm^{-1} in the ligand has been assigned to the carbonyl group C=O. This band is shifted to 1640 cm^{-1} on complex formation of C–O→M (M = Metal) bonding. The strong band at 1650 cm^{-1} in the ligand was assigned to azomethine group. On complex formations this stretching vibration gets lowered to 1635 cm^{-1} indicating the =CH–N–M bond.

Generally the bands below 450 cm^{-1} have been tentatively assigned to metal–oxygen and metal–halogen vibrations[16]. Therefore the new bands appearing in the complex at 425 cm^{-1} and 305 cm^{-1} can be tentatively assigned to Fe–O and Fe–Cl stretching vibrations respectively as suggested by earlier workers[17]. The appearance of these bands suggests the ionic structure $[Fe(C_{24}H_{20}N_2O)_2(Cl_2)]^+(Cl)^-$. On the basis of these experimental facts, the following structure may be suggested for the present complex. Since there is only one M–Cl stretching frequency, it exists in the *trans* form:



References

1 R.C. Saxena and C.L. Jain, *J. of Chem. Eng. and Data* (Accepted).
2 R.C. Saxena, C.L. Jain and S.C. Rastogi, *J. of Inorg. and Nucl. Chem.* (Communicated).
3 L.N. Mulley and P.W. Selwood, *J. Am. Chem. Soc., 76,* 6207 (1954).
4 C.K. Jørgensen, *Acta Chem. Scand., 11,* 73 (1957).
5 C.J. Ballhausen, 'Introduction to Ligand Field Theory', McGraw-Hill, N.Y. (1962), p. 253–255.
6 W. Klen, *Z. Anorg. Chem., 252,* 225 (1944).
7 A.A. Schilt, *J. Am. Chem. Soc., 82,* 3000 (1960).
8 L.M. Venanzi, *J. Chem. Soc.,* 719 (1958).
9 C.K. Jørgensen, *Acta Chem. Scand., 12,* 903 (1958).
10. C.K. Jørgensen and C.E. Schaffer, *'International Symposium on the Chemistry of Co-ordination Compounds', Suppl. Ricerca Scientifica, 8,* 143 (1958).
11 E. Robinowitch and W.H. Stockmayer, *J. Am. Chem. Soc., 64,* 335 (1942).
12 A.V. Kiss, *Z. Anorg. Chem., 99,* 244 (1940).
13 B.N. Figgis 'Introduction to Ligand Fields', Interscience, p. 52.
14 C.S. Naimann, *J. Chem. Phys., 35,* 323 (1961).
15 G. Rosengarten and W. Lon, *J. Mol. Spec., 12,* 319 (1964).
16 K. Nakamoto, 'I.R. Spectra of Inorganic and Coordination Compounds', Wiley, New York.
17 C.C. Prabha Karan and C.C. Patel, *J. Inorg. Nucl. Chem., 32,* 1223 (1970).